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(54) **Aqueous dispersion for chemical mechanical polishing**

(57) The object of the present invention is to provide an aqueous dispersion for chemical mechanical polishing which can be polished working film for semiconductor devices and which is useful for STI. The aqueous dispersion for chemical mechanical polishing of the invention is characterized by comprising an inorganic abrasive such as silica, ceria and the like, and organic particles composed of a resin having anionic group such

as carboxyl group into the molecular chains. The removal rate for silicon oxide film is at least 5 times, particularly 10 times the removal rate for silicon nitride film. The aqueous dispersion may also contain an anionic surfactant such as potassium dodecylbenzene sulfonate and the like. And a base may also be included in the aqueous dispersion for adjustment of the pH to further enhance the dispersability, removal rate and selectivity.

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Description

Background of the Invention

- 5 [0001] The present invention relates to an aqueous dispersion for chemical mechanical polishing. More specifically, it relates to an aqueous dispersion for chemical mechanical polishing that is particularly useful for chemical mechanical polishing of insulating film during the manufacturing steps for semiconductor devices.
- 10 [0002] Improvements in degrees of semiconductor device integration and increased multilayer wiring have led to drastic increases in storage volumes of memory devices. This has been supported by advances in micronization for the working techniques, increased multilayer wiring and the steps for micronization are increasing correspondingly, thus leading to higher chip costs. Given such circumstances, chemical mechanical polishing techniques for polishing of working film and the like have been introduced and attention is being directed toward these techniques. Application of such chemical mechanical polishing techniques has allowed planarization and numerous micronization techniques.
- 15 [0003] One of these micronization techniques is Shallow Trench Isolation, also known as STI. The important factor for the STI technique is the removal rate ratio between the silicon nitride film used as the stopper film and the silicon oxide film, or the "selectivity", and an optimum polishing agent is necessary.

Summary of the Invention

- 20 [0004] In light of the state of the aforementioned STI technique, it is an object of the present invention to provide an aqueous dispersion for chemical mechanical polishing with a high removal rate for silicon oxide film and a low removal rate for silicon nitride film, i.e. a high selectivity.
- [0005] The present invention is as follows.
- 25 1. An aqueous dispersion for chemical mechanical polishing characterized by comprising an inorganic abrasive and organic particles with anionic group, wherein the removal rate for silicon oxide film is at least 5 times the removal rate for silicon nitride film.
 - 30 2. An aqueous dispersion for chemical mechanical polishing according to 1. above, wherein the abovementioned anionic group is at least one selected from among carboxyl group, hydroxyl group, sulfuric acid ester group, sulfonic acid group, phosphoric acid group and epoxy group.
 - 35 3. An aqueous dispersion for chemical mechanical polishing according to 2. above, wherein the abovementioned anionic group is carboxyl.
 4. An aqueous dispersion for chemical mechanical polishing according to any one of 1. to 3. above, wherein the zeta potential of the abovementioned organic particles with the abovementioned anionic group is -10 mV or lower.
 - 40 5. An aqueous dispersion for chemical mechanical polishing according to any one of 1. to 4. above, wherein the abovementioned inorganic abrasive is at least one selected from the group consisting of silica, ceria, alumina, titania and zirconia.
 6. An aqueous dispersion for chemical mechanical polishing according to any one of 1. to 4. above, wherein when the abovementioned inorganic abrasive is silica, the removal rate for silicon oxide film is at least 5 times the removal rate for silicon nitride film.
 - 45 7. An aqueous dispersion for chemical mechanical polishing according to any one of 1. to 5. above, which further comprises an anionic surfactant, wherein when the abovementioned inorganic abrasive is silica, the removal rate for silicon oxide film is at least 6 times the removal rate for silicon nitride film.
 8. An aqueous dispersion for chemical mechanical polishing according to any one of 1. to 4. above, wherein when the abovementioned inorganic abrasive is ceria, the removal rate for silicon oxide film is at least 10 times the removal rate for silicon nitride film.
 - 50 9. An aqueous dispersion for chemical mechanical polishing according to any one of 1. to 5. above, which further comprises an anionic surfactant, wherein when the abovementioned inorganic abrasive is ceria, the removal rate for silicon oxide film is at least 10 times the removal rate for silicon nitride film.
 10. An aqueous dispersion for chemical mechanical polishing according to any one of 1. to 9. above, which is used for a shallow trench isolation step in the manufacture of a semiconductor device.
- 55 [0006] According to the invention, it is possible to obtain an aqueous dispersion for chemical mechanical polishing which is useful for STI steps, to allow polishing of silicon oxide film at an adequate rate while maintaining an adequately high selectivity as the ratio with respect to the removal rate for silicon nitride film, and without producing scratching or dishing.

Detailed Description of the invention

[0007] The aqueous dispersion for chemical mechanical polishing of the invention is characterized by comprising an inorganic abrasive and organic particles with anionic group, wherein the removal rate for silicon oxide film is at least 5 times the removal rate for silicon nitride film.

[0008] The "inorganic abrasive" may be silica, ceria, alumina, titania, zirconia or the like, and particularly preferred are silica and ceria. The silica used may be (1) fumed silica obtained by reacting silicon chloride in the presence of hydrogen and oxygen, (2) colloidal silica obtained by ion-exchange of a silicic acid salt, or (3) colloidal silica obtained by hydrolysis or condensation of a metal alkoxide. The ceria used may be obtained by firing of cerium carbonate, cerium hydroxide or cerium oxalate, but ceria obtained by firing of cerium carbonate is particularly preferred. The inorganic abrasive used may be of a single type, but combinations of two or more, such as silica and ceria, silica and alumina or ceria and alumina may also be used.

[0009] The average particle size of the inorganic abrasive is preferably 0.01-3 μm , because when the average particle size is less than 0.01 μm it is not possible to obtain an aqueous dispersion with an adequately high removal rate. On the other hand, if the average particle size is greater than 3 μm , the inorganic abrasive settles and easily separates, thus making it difficult to achieve a stable aqueous dispersion. The average particle size is more preferably 0.02-1.0 μm , and even more preferably 0.04-0.7 μm . An inorganic abrasive with an average particle size within this range gives a stable aqueous dispersion for chemical mechanical polishing with a high removal rate, and minimal settling or separation of the abrasive. The average particle size can be measured with a dynamic light scattering type measuring instrument, a laser diffraction diffraction type measuring instrument or the like, or it may be measured by observation with a transmission electron microscope. It may also be calculated based on the specific surface area of the powdered inorganic abrasive.

[0010] The content of the inorganic abrasive in the aqueous dispersion will depend on the type of inorganic abrasive, but for silica it may be 2-20 parts by weight (hereunder referred to as "parts"), preferably 4-15 parts and more preferably 6-12 parts, with respect to 100 parts of the aqueous dispersion. If the silica content is less than 2 parts, the removal rate is not adequately improved, and if it is more than 20 parts, the stability of the aqueous dispersion tends to be lower, which is undesirable in terms of cost. For ceria, it may be 0.02-5 parts, preferably 0.05-2 parts and more preferably 0.1-1 part with respect to 100 parts of the aqueous dispersion. The ceria content is preferably not below this range or above this range, because the same problems occur as with silica.

[0011] The "organic particles" with anionic group may be composed of a resin having anionic group introduced into the molecular chains.

[0012] As resin with anionic group introduced into the molecular chains there may be mentioned thermoplastic resin, which include polyvinyl chloride, polystyrene and styrene-based copolymers, polyolefins and polyolefin copolymers such as polyacetals, saturated polyesters, polyamides, polycarbonates, polyethylene, polypropylene, poly-1-butene, poly-4-methyl-1-pentene and the like, as well as phenoxy resin, (meth)acrylic resin such as polymethyl methacrylate, and (meth)acrylic copolymers.

[0013] There may also be mentioned copolymer resin with crosslinked structures obtained by copolymerization of styrene, methyl methacrylate and the like with divinylbenzene, ethylene glycol dimethacrylate and the like. There may also be mentioned thermosetting resin such as phenol resin, urea resin, melamine resin, epoxy resin, alkyd resin and unsaturated polyester resin.

[0014] The organic particles may be produced by any of various methods including emulsion polymerization, suspension polymerization, emulsified dispersion, pulverization or the like. The organic particles used may be of one type or a combination of two or more types.

[0015] The "anionic group" may be functional group that can render the zeta potential of the organic particles negative in the aqueous dispersion, and they are not particularly restricted. Specifically, there may be mentioned carboxyl, hydroxyl group, sulfuric acid ester group, sulfonic group, phosphoric group and epoxy group. Carboxyl group and sulfonic acid group are preferred among these, and carboxyl group is particularly preferred. Organic particles with cationic group result in a relatively lower removal rate for silicon oxide film.

[0016] The zeta potential of the organic particles with the anionic group when measured in the water as same pH as the polishing slurry is -10 mV or lower, and preferably -20 mV or lower. The lower limit is normally -100mV.

[0017] The average particle size of the organic particles is preferably 0.01-3 μm . If the average particle size is less than 0.01 μm , the ratio of the removal rate for silicon oxide film with respect to the removal rate for silicon nitride film is reduced, such that the selectivity may not be improved. On the other hand, if the average particle size is greater than 3 μm , the organic particles settle and easily separate, thus making it difficult to achieve a stable aqueous dispersion. The average particle size is more preferably 0.02-1.0 μm , and even more preferably 0.04-0.7 μm . Organic particles with an average particle size within this range result in a stable aqueous dispersion for chemical mechanical polishing with a high selectivity, and minimal settling or separation of the particles. The average particle size can be measured in the same manner as for the inorganic abrasive.

[0018] The organic particle content in the aqueous dispersion will depend on the type and the average particle size of the inorganic abrasive, but in the case of a silica inorganic abrasive it may be 0.05-10 parts, preferably 0.1-5 parts and more preferably 0.2-3 parts, with respect to 100 parts of the aqueous dispersion. If the organic particle content is less than 0.05 part, the selectivity is not adequately improved, and if it is more than 10 parts, the stability of the aqueous dispersion tends to be lower, which is undesirable in terms of cost. In the case of a ceria inorganic abrasive, the organic particle content may be 0.02-5 parts, preferably 0.05-2 parts and more preferably 0.1-1 part with respect to 100 parts of the aqueous dispersion. The organic particle content is preferably not below this range or above this range, because the same problems occur as with a silica inorganic abrasive.

[0019] The inorganic abrasive and organic particles do not necessarily need to be dispersed in a mutually independent state. For example, an alkoxysilane may be polycondensed together with the inorganic abrasive and organic particles, with the polysiloxane bonded to at least the surface of the organic particles, and with the inorganic abrasive such as silica or ceria also bonded by electrostatic force. The resulting polysiloxane in this case may be directly bonded to the anionic group of the organic particles, or it may be indirectly bonded through a silane coupling agent or the like.

[0020] The medium for the aqueous dispersion may be water or a mixed medium composed mostly of water, such as a mixture of water and methanol, but water alone is particularly preferred.

[0021] The aqueous dispersion for chemical mechanical polishing according to the invention comprises an inorganic abrasive, organic particles and water, to provide a polishing agent with high selectivity and excellent performance, which can be used in STI steps for manufacture of semiconductor devices. With conventionally used silica, the selectivity is about 2-3, but according to the invention, the use of a combination of organic particles with anionic group and silica allows a selectivity of 5 or more. When ceria is used as the inorganic abrasive or the conditions are optimized, the selectivity can be increased to 10 or more, 20 or more and even 30 or more.

[0022] It is also possible to increase the selectivity by further including an anionic surfactant. For example, when silica is used as the inorganic abrasive, the selectivity can be increased to 6 or more. When ceria is used as the inorganic abrasive, the selectivity can be increased to 10 or more, 20 or more and even 30 or more.

[0023] The aqueous dispersion of the invention may also include various additives to further enhance its performance.

[0024] By adding an acid it is possible to stabilize the aqueous dispersion, which will further increase the selectivity in some cases. The acid is not particularly restricted, and any organic acid or inorganic acid may be used. As organic acids there may be mentioned para-toluenesulfonic acid, dodecylbenzenesulfonic acid, isoprenesulfonic acid, gluconic acid, lactic acid, citric acid, tartaric acid, malic acid, glycolic acid, malonic acid, formic acid, oxalic acid, succinic acid, fumaric acid, maleic acid, phthalic acid and the like. As inorganic acids there may be mentioned nitric acid, hydrochloric acid, sulfuric acid and the like. These organic acids or inorganic acids may be used alone or in combinations of two or more, and organic acids and inorganic acids may also be used together. These acids may be included at 0.02-2 parts and especially 0.05-1 part with respect to 100 parts of the aqueous dispersion.

[0025] A base may also be included in the aqueous dispersion for adjustment of the pH to further enhance the dispersability, removal rate and selectivity. The pH is not particularly restricted but will normally be about 5-12 and preferably 6-11. The base is also not particularly restricted, and any organic or inorganic base may be used. As organic bases there may be mentioned nitrogen-containing organic compounds such as ethylenediamine, ethanolamine and the like. As inorganic bases there may be mentioned ammonia, potassium hydroxide, sodium hydroxide, lithium hydroxide and the like, and these bases may be used alone or in combinations of two or more. The content of these bases is important for adjustment of the pH, but they may be added at 0.01-1 part and especially 0.02-0.5 part with respect to 100 parts of the aqueous dispersion. The preferred pH will differ depending on the inorganic abrasive, and in the case of silica the pH is preferably 10-12, while in the case of ceria the pH is preferably 5-12; these pH ranges are preferred to allow both enhanced removal rate and selectivity.

[0026] The aqueous dispersion may also contain, as additional additives, oxidizing agents, polyvalent metal ions, surfactants and the like.

[0027] As oxidizing agents, hydrogen peroxide, peroxosulfate, heteropolyacid and the like can be used. As polyvalent metal ions, aluminium, titan, chromium, vanadium and the like can be used.

[0028] The surfactants may be anionic surfactant, nonionic surfactant, cationic surfactant or amphoteric surfactant, but anionic surfactant are preferred. As examples of anionic surfactant there may be mentioned potassium dodecylbenzene sulfonate, ammonium dodecyl sulfate and the like. The contents of these anionic surfactant may be 0 to 0.5 wt%, preferably 0.005 to 0.2 wt% and more preferably 0.01 to 0.1 wt% with respect to the aqueous dispersion.

[0029] There may also be added dispersing agents such as polyacrylic acid and viscosity adjustors such as polyacrylamide.

[0030] In the aqueous dispersion of the invention, the aforementioned additives are combined with the inorganic abrasive and the organic particles with anionic group as necessary, to allow further enhancement of the selectivity in STI steps.

[0031] When an aqueous dispersion for chemical mechanical polishing according to the invention is used for chemical mechanical polishing of a polishing surface, the polishing may be carried out under prescribed conditions using a

commercially available chemical mechanical polishing apparatus (for example, Model "EPO-112" and "EPO-222" by Ebara Corporation, Model "LGP510" or "LGP552" by Lapmaster SFT Co., Ltd.; Article name "Mirra" by Applied Materials Corp.; Article name "Teres" by Lam Research Corp. and Model "AVANTI 472" by Speed Fam-IPEC Corp.).

Description of the Preferred Embodiments

[0032] The present invention will now be explained in further detail by way of examples.

(1) Synthesis of organic particles

Synthesis Example 1 [Synthesis of organic particles: Anionic polymethyl methacrylate (anionic PMMA) particles]

[0033] After loading 96 parts of methyl methacrylate, 4 parts of methacrylic acid, 0.1 part of ammonium lauryl sulfate, 0.5 part of ammonium persulfate and 400 parts of ion-exchange water into a 2-liter flask, the temperature was raised to 70°C while stirring in a nitrogen gas atmosphere, for 6 hours of polymerization. This yielded an aqueous dispersion comprising carboxyl group- and sulfuric acid ester group-containing anionic PMMA particles with an average particle size of 0.2 µm. The polymerization yield was 95%, and the carboxyl group distribution as measured by conductometric titration was 40% inside the particles, 50% on the particle surfaces and 10% in the aqueous phase. The zeta potential was -25 mV as measured with a laser Doppler electrophoresis light scattering zeta potential meter (Type "DELSA440" by COULTER Corp.).

Synthesis Example 2 [Synthesis of organic particles: Anionic polystyrene (anionic PS) particles]

[0034] After loading 96 parts of styrene, 4 parts of methacrylic acid, 0.1 part of ammonium lauryl sulfate, 0.5 part of ammonium persulfate and 400 parts of ion-exchange water into a 2-liter flask, the temperature was raised to 80°C while stirring in a nitrogen gas atmosphere, for 12 hours of polymerization. This yielded an aqueous dispersion comprising carboxyl group- and sulfuric acid ester group-containing anionic PS particles with an average particle size of 0.2 µm. The polymerization yield was 95%, and the carboxyl group distribution as measured by conductometric titration was 40% inside the particles, 50% on the particle surfaces and 10% in the aqueous phase. The zeta potential was -36 mV as measured in the same manner as Synthesis Example 1.

Comparative Synthesis Example 1 [Synthesis of cationic PMMA particles]

[0035] After loading 95 parts of methyl methacrylate, 5 parts of 4-vinylpyridine, 2 parts of an azo-based polymerization initiator (trade name "V50" by Wako Junyaku Co., Ltd.) and 400 parts of ion-exchange water into a 2-liter flask, the temperature was raised to 70°C while stirring in a nitrogen gas atmosphere, for 8 hours of polymerization. This yielded amino group-containing cationic PMMA particles with an average particle size of 0.2 µm. The polymerization yield was 96%. Comparative Synthesis Example 2 [Synthesis of cationic PS particles]

[0036] After loading 95 parts of styrene, 5 parts of 4-vinylpyridine, 2 parts of an azo-based polymerization initiator (trade name "V50" by Wako Junyaku Co., Ltd.) and 400 parts of ion-exchange water into a 2-liter flask, the temperature was raised to 75°C while stirring in a nitrogen gas atmosphere, for 14 hours of polymerization. This yielded amino group-containing cationic PS particles with an average particle size of 0.2 µm. The polymerization yield was 94%.

(2) Aqueous dispersion containing silica as inorganic abrasive, and chemical mechanical polishing employing the same

Example 1

[0037] An aqueous dispersion was prepared by adding the anionic PMMA particles of Synthesis Example 1 in an amount of 2 wt% to an aqueous dispersion containing 10 wt% fumed silica (#90, product of Nihon Aerosil Co., Ltd.) and 0.2 wt% KOH.

[0038] This aqueous dispersion was used for chemical mechanical polishing under the following conditions.

[0039] A 1000 nm thick thermal silicon oxide film and a 200 nm thick silicon nitride blanket wafer were set in a chemical mechanical polishing apparatus (Model "EPO-112", product of Ebara Corporation). A porous polyurethane polishing pad (product name: "IC1000" by Rodel-Nitta Corp.) was used for polishing of a urethane pad surface for 3 minutes under a load of 300 g/cm², with a table rotation rate of 50 rpm and a head rotation rate of 50 rpm while supplying the aforementioned aqueous dispersion at a rate of 200 cc/min. As a result, the removal rate on the silicon oxide film was 144 nm/min while the removal rate on the silicon nitride blanket wafer was 28.2 nm/min. Thus, the selectivity was adequately high at 5.1, and no scratches were produced, thus demonstrating that the aqueous dispersion has adequate

performance for STI steps.

[0040] The number of scratches was measured with a non-patterned wafer surface foreign matter scanning apparatus ("Surfacescan 6420", product of KLA Tencor Co., Ltd.) after polishing an 8-inch thermal oxidation wafer for 2 minutes in the same manner. The numbers of scratches in the following examples and comparative examples were measured

Examples 2-7 and Comparative Examples 1-4

[0041] The removal rates and numbers of scratches on thermal silicon oxide film and silicon nitride blanket wafers were evaluated in the same manner as Example 1, using the types of silica, organic particles and additives shown in Table 1.

[0042] In Table 1, DBS-K is dodecylbenzenesulfonic acid potassium salt, PAA-K is polyacrylic acid potassium salt (molecular weight: 25,000), and IPS-K is polyisoprenesulfonic acid potassium salt (molecular weight: 8000). The colloidal silica used was prepared by solvent replacement of water in a condensate of tetraethoxysilane in an ethanol/water mixed solvent using ammonia as the catalyst, as described in J. of Colloid and Interface Science, 25, 62-69 (1968). Particle size control was accomplished by adjusting the ethanol and water composition.

[0043] The results are listed in Table 1 together with the results for Example 1.

[0044] According to Table 1, the removal rates in Examples 1 to 7 were adequate at 101 nm/min or more, and the selectivities were also 5.1 or more, indicating them to be useful as aqueous dispersions for STI steps. Also, virtually no scratches were observed, indicating excellent polishing. On the other hand, the selectivities in Comparative Examples 1 and 4 were low at 2.8 and 2.6, respectively, such that they cannot be used as aqueous dispersions for STI steps, and the selectivities in Comparative Examples 2 and 3 were even lower and the removal rates were low, demonstrating that they are not suitable for practical use.

Table 1

		Inorganic abrasive	Organic particles		Additive (0.02 wt%)	SiO ₂ removal rate (nm/min)	Si ₃ N ₄ removal rate (nm/min)	Selec- tivity	Scratches (number)
		Type/content	Type/content	Zeta potential					
Examples	1	#90 fumed silica/10	Anionic PMMA/2	-25	—	144	28.2	5.1	0
	2				DBS-K	123	19.5	6.3	
	3				PAA-K	107	13.5	7.9	
	4				ISP-K	119	20.1	5.9	
	5				—	139	25.3	5.5	
	6	20 nm colloidal silica/10			—	129	22.2	5.8	
	7	90 nm colloidal silica/10			PAA-K	101	11.2	8.9	
Comparative Examples	1	#90 fumed silica/10	—	—	—	149	52.0	2.8	0
	2		Cationic PMMA/2	+14		29	15.2	1.9	6
	3		Cationic PS/2	+18		19	14.6	1.3	19
	4		—	—		112	43.6	2.6	0

(3) Aqueous dispersion containing ceria as inorganic abrasive, and chemical mechanical polishing employing the same

Example 8

[0045] Using bastnaesite as the starting material, this was subjected to alkali treatment and then dissolved in nitric acid and subjected to extraction with an organic solvent to remove the impurities, and then after dissolution in nitric

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acid, it was recrystallized 3 times as a carbonate salt to obtain a highly pure carbonate salt of cerium. This was fired at 900°C to obtain ceria. The ceria was dispersed in ion-exchange water to a content of 0.3 wt%, and the pH was adjusted to 6.5 with ammonia to obtain an aqueous dispersion containing ceria with an average particle size of 0.24 µm. Next, the anionic PMMA particles of Synthesis Example 1 were added to a content of 0.7 wt%, to prepare an aqueous dispersion.

[0046] This aqueous dispersion was used to evaluate the removal rates on a thermal silicon oxide film and silicon nitride blanket wafer in the same manner as Example 1, except that the load was 250 g/cm² and the polishing time was 3 minutes. As a result, the removal rate on the silicon oxide film was 299 nm/min while the removal rate on the silicon nitride blanket wafer was 13.6 nm/min. Thus, the selectivity was adequately high at 22, and no scratches were produced, thus demonstrating the aqueous dispersion to have adequate performance for STI steps.

Examples 9-16 and Comparative Examples 5-10

[0047] The removal rates and numbers of scratches on thermal silicon oxide film and silicon nitride blanket wafers were evaluated in the same manner as Example 8, using the ceria concentrations, the types and concentrations of organic particles and the types of additives shown in Table 2.

[0048] The DBS-K, PAA-K and IPS-K in Table 2 are the same as in Table 1.

[0049] The results are listed in Table 2 together with the results for Example 8.

[0050] According to Table 2, the removal rates in Examples 8 to 16 were adequately high at 245 nm/min or more, and the selectivities were also adequately high at 22 or more. Also, no scratches were observed, indicating excellent polishing. On the other hand, the selectivities in Comparative Examples 5, 8, 9 and 10 were low and numerous scratches were found, demonstrating that they are not suitable for STI use. In Comparative Examples 6 and 7, the insufficient removal rate on the silicon oxide film and numerous scratches constituted a problem.

Table 2

	Inorganic abrasive	Organic particles		Additive (0.01 wt%)	pH	SiO ₂ removal rate (nm/min)	Si ₃ N ₄ removal rate (nm/min)	Selectivity	Scratches (number)	
		Type/content	Zeta potential							
Examples	8	Cerla/0.3	Anionic PMMA/0.7	-25	6.5	299	13.6	22	0	
	9					258	8.9	24		
	10					277	9.6	29		
	11					245	7.9	31		
	12					332	11.5	29		
	13	Cerla/1	Anionic PS/0.7	-36		349	13.4	26		
14	Cerla/2	Anionic PMMA/2	398			12.4	32			
15	Cerla/0.3	Anionic PMMA/4	379			17.2	22			
16		Anionic P PMMA/0.7	328	12.1	27					
Comparative Examples	5	Cerla/0.3	—	—	10.5	308	52.2	5.9		9
	6					Cationic PMMA/0.7	93	20.7	4.5	3
	7					Cationic PS/0.7	83	28.6	2.9	4
	8					—	258	21.3	12.1	2
	9						341	59.1	5.8	3
	10	PAA-K	281	31.1			9	2		

[0051] The object of the present invention is to provide an aqueous dispersion for chemical mechanical polishing which can be polished working film for semiconductor devices and which is useful for STI. The aqueous dispersion for chemical mechanical polishing of the invention is characterized by comprising an inorganic abrasive such as silica, ceria and the like, and organic particles composed of a resin having anionic group such as carboxyl group into the molecular chains. The removal rate for silicon oxide film is at least 5 times, particularly 10 times the removal rate for silicon nitride film. The aqueous dispersion may also contain an anionic surfactant such as potassium dodecylbenzene

sulfonate and the like. And a base may also be included in the aqueous dispersion for adjustment of the pH to further enhance the dispersability, removal rate and selectivity.

5 Claims

1. An aqueous dispersion for chemical mechanical polishing **characterized by** comprising an inorganic abrasive and organic particles with anionic group, wherein the removal rate for silicon oxide film is at least 5 times the removal rate for silicon nitride film.
2. An aqueous dispersion for chemical mechanical polishing according to claim 1, wherein said anionic group is at least one selected from among carboxyl group, hydroxyl group, sulfuric acid ester group, sulfonic acid group, phosphoric acid group and epoxy group.
3. An aqueous dispersion for chemical mechanical polishing according to claim 2, wherein said anionic group is carboxyl.
4. An aqueous dispersion for chemical mechanical polishing according to any one of claims 1 to 3, wherein the zeta potential of said organic particles with said anionic group is -10 mV or lower.
5. An aqueous dispersion for chemical mechanical polishing according to any one of claims 1 to 4, wherein said inorganic abrasive is at least one selected from the group consisting of silica, ceria, alumina, titania and zirconia.
6. An aqueous dispersion for chemical mechanical polishing according to any one of claims 1 to 4, wherein when said inorganic abrasive is silica, the removal rate for silicon oxide film is at least 5 times the removal rate for silicon nitride film.
7. An aqueous dispersion for chemical mechanical polishing according to any one of claims 1 to 5, which further comprises an anionic surfactant, wherein when said inorganic abrasive is silica, the removal rate for silicon oxide film is at least 6 times the removal rate for silicon nitride film.
8. An aqueous dispersion for chemical mechanical polishing according to any one of claims 1 to 4, wherein when said inorganic abrasive is ceria, the removal rate for silicon oxide film is at least 10 times the removal rate for silicon nitride film.
9. An aqueous dispersion for chemical mechanical polishing according to any one of claims 1 to 5, which further comprises an anionic surfactant, wherein when said inorganic abrasive is ceria, the removal rate for silicon oxide film is at least 10 times the removal rate for silicon nitride film.
10. An aqueous dispersion for chemical mechanical polishing according to any one of claims 1 to 9, which is used for a shallow trench isolation step in the manufacture of a semiconductor device.



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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 0 846 740 A (IBM) 10 June 1998 (1998-06-10) * page 6, line 44 - line 58 *	1,2,5-10	C09G1/02 H01L21/3105 C09K3/14
X	WO 99 64527 A (RODEL HOLDINGS INC) 16 December 1999 (1999-12-16) * claims 1-3 *	1-3,5,6, 8,10	
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 14, 22 December 1999 (1999-12-22) -& JP 11 246852 A (SONY CORP), 14 September 1999 (1999-09-14) * abstract *	1-3,5,6, 8,10	
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 558 (C-1264), 25 October 1994 (1994-10-25) -& JP 06 199917 A (MITSUI TOATSU CHEM INC), 19 July 1994 (1994-07-19) * abstract * * paragraph '0010! - paragraph '0014! *	1-3,5-7, 10	
X	EP 0 823 450 A (MITSUBISHI RAYON CO) 11 February 1998 (1998-02-11) * examples 1,3 *	1,2,5,6, 10	TECHNICAL FIELDS SEARCHED (Int.Cl.7) H01L C09G C09K
X	US 4 777 153 A (AKSAY ILHAN A ET AL) 11 October 1988 (1988-10-11) * column 5, line 10 - column 7 *	1,5,7,10	
A	PATENT ABSTRACTS OF JAPAN vol. 012, no. 075 (C-480), 9 March 1988 (1988-03-09) -& JP 62 213839 A (HOECHST GOSEI KK), 19 September 1987 (1987-09-19) * abstract *	1-10	
The present search report has been drawn up for all claims			
Place of search: THE HAGUE		Date of completion of the search: 8 October 2003	Examiner: Szarowski, A
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
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EUROPEAN SEARCH REPORT

Application Number
EP 01 11 2145

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
P,X	EP 1 036 836 A (JSR CORP ; TOKYO SHIBAURA ELECTRIC CO (JP)) 20 September 2000 (2000-09-20) * the whole document *	1-10	
P,X	EP 1 020 488 A (JSR CORP ; TOKYO SHIBAURA ELECTRIC CO (JP)) 19 July 2000 (2000-07-19) * the whole document *	1-10	
P,X	EP 1 020 501 A (JSR CORP ; TOKYO SHIBAURA ELECTRIC CO (JP)) 19 July 2000 (2000-07-19) * the whole document *	1-10	
P,X	EP 1 081 200 A (JSR CORP) 7 March 2001 (2001-03-07) * the whole document *	1-6,8,10	
E	EP 1 104 778 A (JSR CORP) 6 June 2001 (2001-06-06) * the whole document *	1-10	
E	EP 1 243 611 A (JSR CORP) 25 September 2002 (2002-09-25) * the whole document *	1-10	
E	EP 1 123 956 A (JSR CORP) 16 August 2001 (2001-08-16) * the whole document *	1-10	
E	EP 1 116 762 A (JSR CORP) 18 July 2001 (2001-07-18) * the whole document *	1-10	
E	EP 1 138 734 A (JSR CORP) 4 October 2001 (2001-10-04) * the whole document *	1-10	
-/--			
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		8 October 2003	Szarowski, A
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.82 (P4/C01)



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EUROPEAN SEARCH REPORT

Application Number
EP 01 11 2145

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CI.7)
E	EP 1 138 733 A (JSR CORP) 4 October 2001 (2001-10-04) * the whole document *	1-10	
			TECHNICAL FIELDS SEARCHED (Int.CI.7)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 8 October 2003	Examiner Szarowski, A
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03 B2 (P04001)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 11 2145

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

08-10-2003

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0846740	A	10-06-1998	US 5876490 A	02-03-1999
			EP 0846740 A1	10-06-1998
			JP 3130279 B2	31-01-2001
			JP 10168431 A	23-06-1998
			TW 420716 B	01-02-2001
WO 9964527	A	16-12-1999	EP 1102821 A1	30-05-2001
			JP 2002517593 T	18-06-2002
			WO 9964527 A1	16-12-1999
			US 6331134 B1	18-12-2001
			US 2003181046 A1	25-09-2003
			US 2002019202 A1	14-02-2002
			US 2001024933 A1	27-09-2001
JP 11246852	A	14-09-1999	NONE	
JP 06199917	A	19-07-1994	NONE	
EP 0823450	A	11-02-1998	EP 0823450 A1	11-02-1998
			US 5939471 A	17-08-1999
			CN 1187833 A , B	15-07-1998
			WO 9634036 A1	31-10-1996
			JP 2877520 B2	31-03-1999
US 4777153	A	11-10-1988	CA 1317316 C	04-05-1993
			WO 9003349 A1	05-04-1990
JP 62213839	A	19-09-1987	JP 1914457 C	23-03-1995
			JP 6040951 B	01-06-1994
EP 1036836	A	20-09-2000	JP 2000269169 A	29-09-2000
			JP 2000273311 A	03-10-2000
			JP 2000269170 A	29-09-2000
			EP 1036836 A1	20-09-2000
EP 1020488	A	19-07-2000	JP 2000204352 A	25-07-2000
			JP 2000204355 A	25-07-2000
			EP 1020488 A2	19-07-2000
			KR 2000053505 A	25-08-2000
			US 6454819 B1	24-09-2002
EP 1020501	A	19-07-2000	JP 2000204353 A	25-07-2000
			JP 2000208452 A	28-07-2000
			JP 2000204275 A	25-07-2000
			EP 1020501 A2	19-07-2000
			KR 2000053504 A	25-08-2000

EPO FORM P0455

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 11 2145

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

08-10-2003

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1020501	A		US. 6375545 B1	23-04-2002
EP 1081200	A	07-03-2001	JP 2001077062 A	23-03-2001
			EP 1081200 A1	07-03-2001
			US 6447695 B1	10-09-2002
EP 1104778	A	06-06-2001	JP 2001152135 A	05-06-2001
			JP 2001152133 A	05-06-2001
			EP 1104778 A2	06-06-2001
			EP 1243611 A1	25-09-2002
			US 6582761 B1	24-06-2003
EP 1243611	A	25-09-2002	JP 2001152135 A	05-06-2001
			JP 2001152133 A	05-06-2001
			EP 1243611 A1	25-09-2002
			EP 1104778 A2	06-06-2001
			US 6582761 B1	24-06-2003
EP 1123956	A	16-08-2001	EP 1123956 A1	16-08-2001
			JP 2002080827 A	22-03-2002
			US 2001039766 A1	15-11-2001
EP 1116762	A	18-07-2001	JP 2001196336 A	19-07-2001
			JP 2002121541 A	26-04-2002
			EP 1116762 A1	18-07-2001
			US 2001008828 A1	19-07-2001
EP 1138734	A	04-10-2001	JP 2001279231 A	10-10-2001
			EP 1138734 A2	04-10-2001
			US 2002005017 A1	17-01-2002
EP 1138733	A	04-10-2001	JP 2001269859 A	02-10-2001
			EP 1138733 A2	04-10-2001
			US 2001049912 A1	13-12-2001

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82